

Lamont Geological Observatory

Columbia University

PALISADES, NEW YORK
GEOCHEMICAL LABORATORY

Handwritten notes:
The 1957
+ missing

Holder 26

Technical Report No. 4
(Contract N6 onr 271 Task Order 18)

Age of Deep Ocean Water

Lamont Geological Observatory
(Columbia University)
Palisades, New York.

Age of Deep Ocean Water

Technical Report No.4

by

J. Laurence Kulp

The research reported in this document has been made possible through support and sponsorship extended by the United States Navy, Office of Naval Research and the Geophysical Research Directorate of the Air Force Cambridge Research Laboratories under Contract AF19(122)214. The Cooperation of the Woods Hole Oceanographic Institution and the United States Navy Hydrographic Office in the sample procurement from the "ATLANTIS" and "SAN PABLO" respectively is greatly appreciated.

December 1951

TABLE OF CONTENTS

	<u>Page</u>
Abstract	1
Introduction	2
Method	4
Experimental Techniques	4
Water Sampling	4
CO ₂ Extraction	4
Carbon preparation	6
Cl ¹⁴ Counting	6
Calibration	7
Results	8
Discussion	9
Bibliography	12



Digitized by the Internet Archive
in 2020 with funding from
Columbia University Libraries

<https://archive.org/details/ageofdeepoceanwa00kulp>

ABSTRACT

275 gallon water samples from the surface and the ocean bottom have been taken, the carbon dioxide removed, converted to carbon and counted for the natural carbon 14 concentration. This permits measurement of the apparent time since the water left the surface and hence indicates the rate of deep water circulation. One sample west of the mid-Atlantic Ridge at latitude 58° N gave an age of 1600 ± 130 years while one on the east side at about latitude 53° gave 1750 ± 150 years. The results on these preliminary samples show that the ocean circulation is on a scale of thousands of years rather than tens of years. This has important implications for oceanography, meteorology and geophysics.

INTRODUCTION

Contract N6onr271 T.O.18 has as its objective the age measurement of deep ocean materials. One of the most important and least known parameters in oceanography is the rate of deep ocean circulation. A method has been developed which can quantitatively determine the rate as well as the direction of deep sea circulation. This technical report describes this method and gives the preliminary results obtained by its application.

The method depends on the measurement of the concentration of carbon 14 in the water at any given location. As long as the water is in equilibrium with the atmosphere, the carbon 14 concentration remains constant since it is continuously produced in the upper atmosphere by cosmic ray bombardment (Anderson & Libby, 1951) and thus enters the CO₂-air-water-life cycle. When surface water descends it is cut off from the source of supply and thus the carbon 14 concentration decreases according to the half life. In general the cold polar water sinks, moves along the bottom toward the equator where it presumably returns to the surface. Therefore if the water on the bottom is sampled at any particular location, and the carbon 14 concentration measured, the time since the water left the surface can be approximately ascertained.

In order to achieve these results a great deal of planning and effort was required by a considerable number of men. Different assistants were involved in the sampler engineering and construction, sample taking, chemical processing, and counting. The first samples were taken in the summer of 1950 on a cruise of the "ATLANTIS" under the direction of Professor Maurice Ewing. The amount of carbon obtained was inadequate for a precision C_{14} measurement but the count did suggest that the water was measurably old. With this encouragement, two new model water samplers were constructed, the chemical process was intensively studied on a pilot plant scale, to improve efficiency, and new cruises planned. During the summer of 1951 one sampler was placed on a cruise of the Woods Hole vessel "ATLANTIS" and another was placed on the U.S. Hydrographic Office vessel "SAN PABLO". The "ATLANTIS" cruise encountered very poor weather and the sampler developed numerous mechanical difficulties so that only one good surface water sample was obtained. The sampler on the "SAN PABLO" worked well but after two excellent deep water samples were taken, the sampler was lost.

The construction of another new model sampler has been completed for the "SAN PABLO" which is to leave for a cruise in January 1952. If this sampler is satisfactory it is hoped that such equipment can be made standard on several ships so that the potentially important results can be accumulated as rapidly as possible.

METHOD

The first step is the procurement of the large water sample (~ 275 gallons) in a container which is essentially air-tight. This is then brought on deck, sulfuric acid is added to the water to convert the carbonate and bicarbonate to CO₂ which is swept through an absorption train by a stream of CO₂ - free nitrogen. The absorbed CO₂ is released in the laboratory by the addition of acid and after purification is reduced to pure carbon. This is mounted in a special Geiger tube and counted.

EXPERIMENTAL TECHNIQUES

A. Water Sampling

In order to obtain an adequate sample for counting, eight grams of carbon is necessary. In the first attempt at deep water sampling, (1950 cruise) a 100 gallon sampler was used which yielded samples of about 4 grams each. This was probably only a 50% yield. Since the "SAN PABLO" had sufficient equipment to handle a much larger sampler it was decided to use a 275 gallon oil tank as the container. Figures 1, 2, and 3 show the details of this sampler. It was attached on the main cable about 100' above the coring rig. The sampler is sent down with the top and bottom parts open. When the coring rig hits bottom the lids are triggered so that they close due to tension of the springs attached to the inside of the sampler.

B. CO₂ EXTRACTION

A carbon yield of better than 90% can be obtained by the following procedure: about 3 liters of deep water are drained from

the sampler and preserved for salinity pH, and possible isotopic analyses. 3 liters of concentrated sulphuric acid are then added which produce a pH of about 1 and convert all of the carbonate and bicarbonate to CO_2 . A flow of CO_2 -free nitrogen is then introduced at the bottom of the sampler. The nitrogen comes up through the water, picks up the CO_2 and carries it into the absorption train which is connected to the top of the sampler. The absorption train consists consecutively of three bubblers containing concentrated sulphuric acid to remove water, a tube containing 1 lb. of ascarite to remove the CO_2 and a flow meter.

It was shown in pilot plant experiments that the rate of CO_2 removal by the ascarite is very fast and is quantitative so that the rate of nitrogen flow is not critical. The total volume of nitrogen used, however, is quite critical. Table 1 shows the volume of nitrogen required for a certain % CO_2 removal from 50 liters of water containing initially about the same carbonate concentration as sea water.

TABLE I.

<u>Value Nitrogen at 1 atm, 25°C</u>	<u>% CO_2 recovered</u>
0 liter	0
112	47
225	75
330	97
450	100

It appears that 6-8 times the volume of the sampler is required for high yield. Since a flow of ten liters per minute is feasible, the sweeping process requires about two hours. After the run is completed, the ascarite tube is sealed and sent to the laboratory.

C. Carbon Preparation

The details of the carbon preparation are given elsewhere (Kulp, Tryon and Feely, 1952). In brief, the CO_2 is released from the ascarite by HCl , dried and condensed with liquid air. It is then pumped on and subsequently expanded into a concentrated ammonia solution from which it is precipitated as Ca CO_3 . The Ca CO_3 is thoroughly washed. It is then acidified and the pure CO_2 trapped at liquid air temperature from which position it is expanded and reduced over hot magnesium metal contained in an iron tube. The excess magnesium and magnesium oxide are leached away leaving a pure carbon with less than 1% ash content. A water-carbon slurry is made of this product which is coated inside an 8" length of a 16" long stainless steel sample cylinder and the complete cylinder placed inside a 24" long screen wall Geiger counter which has a central active length of 8". Thus if the sample cylinder is at one end of the counter, the carbon sample is counted while, if it is at the other end, the blank cylinder is counted (background).

D. Carbon 14 Counting

The details of the counting techniques are also given elsewhere (Kulp, Tryon and Feely, 1952; Kulp and Tryon, 1952). The major problem involved is created by the extremely low concentration of C^{14} in nature and the soft character of its beta radiation. To count this isotope in such low concentrations the background due to natural gamma radiation and cosmic rays must be reduced to a very low value. This is accomplished by shielding the counter with

8" of iron in all directions. The dual iron shield in use at the Lamont Observatory weighs 12 tons. This shield absorbs essentially all natural gamma rays as well as soft cosmic ray components. In order to eliminate the background due to the hard cosmic rays, a ring of anticoincidence counters are placed around the screen wall Geiger counter. The electronic circuit is then arranged so that whenever a pulse occurs in the sample counter and one in the ring of counters at the same instant, that pulse is cancelled. By these devices the background can be reduced from about 400 cpm to about 6 cpm. Further, by inserting a 1" mercury shield between the anticoincidence ring and the screen wall counter most of the gammas generated in the iron shield itself may be eliminated bringing the background down to about 2-3 cpm.

The actual C14 count is determined by difference of the carbon and background minus the background. The sample cylinder is changed about once every four hours for three days in order to obtain enough total counts to reduce the statistical error to a reasonable value (1% for modern carbon).

E. Calibration

Calibration has been done with samples of known age such as historical objects, tree rings or known carbon mixtures. In all cases the carbon 14 age has agreed with the known age.

Interlaboratory checks between Prof. Libby's laboratory at the University of Chicago and the Lamont Observatory laboratory have been satisfactory.

Anthracite and modern wood or shell samples are run frequently to check the possibility of contamination. The system now in use seems to be consistently free of such contamination. In the past where traces of contamination appeared, it has always been introduced after the carbon was prepared. It should also be emphasized that any laboratory contamination will tend to make the age appear too young. Nothing in the laboratory procedure can make the sample too old. This is particularly important in considering the reliability of the deep ocean water dates.

RESULTS

The essential results of the deep water age work are summarized in Table 2. The deep sample at 58° latitude was taken west of the mid-Atlantic Ridge while the sample at 53° latitude was taken east of the mid-Atlantic Ridge. Each sample was counted three separate times against background with the net count shown in Table 2. Between each of these counts the sample was released, dried and bottled. The results are quite self-consistent. The value for the surface sample is the same as modern shell. This result was not unexpected but it was necessary to confirm the assumption of the constancy of similar carbon bearing materials in contact with the CO₂ cycle. The deep samples are far outside the experimental error which is certainly not much greater than the probable error as shown. The results give 1600 ± 130 years for the 58° latitude sample while the 53° latitude sample gives 1750

± 150 years.

In order to check this important result further, a direct comparison experiment was set up. The surface sample was mounted in one side of the sample cylinder while the deep water carbon from 58° latitude was mounted on the other. Thus a direct comparison in the difference between the two count rates was available. As is seen in Table 2, this difference by direct measurement against background is the same as that obtained by comparison measurements in the same counter. This increases the confidence in the conclusion that there is a real difference equivalent to 1600 to 1700 years in the count rate of the carbon from the deep water and the surface water at this latitude and topographic position.

DISCUSSION

The result shown in Table 2 must be interpreted. An immediate question arises as to whether the apparent age of the deep water is due to some other factor than simply the time since the water was at the surface. The lower Cl_4 content of the bottom water could conceivably be due to solution of older limestone along the bottom. This alternative is unsatisfactory for several reasons.

(1) Surface carbonate in several cores has yielded recent count.

(2) The cold bottom water from either the Antarctic or Arctic is saturated with carbonate at the surface and actually gets warmer in transit thus making it supersaturated so that the process would be one of precipitation rather than solution.

(3) The carbonate content of the bottom in the region where these samples were taken is relatively small.

It is concluded that these dates are real and that they show the deep ocean circulation to take place on a scale of thousands rather than tens of years as previously thought. (Kuenen, 1950). Obviously dozens, if not hundreds of measurements must be made before any comprehensive description of the rate and direction of ocean circulation can be made. However the technique is now available.

Such slow movement of the bottom water affects most oceanographic theory. For the first time some quantitative estimate of the rate of movement may be made. Further, this slow movement is an independent argument for the absence of granite under the ocean basins. It has been calculated by Anderson and Libby (1951) and Kiersted (1951) that if one assumes the rate of heat flow from the ocean floor to be equal to that of the continents and if the circulation rate is on a scale of thousands of years, turbulence and a temperature inversion near the bottom should be observed. Since no such inversion is apparent, and the rate of circulation is indeed on a time scale of thousands of years, the heat flow must be an order of magnitude less than these calculations indicate. This means in turn that rocks are basaltic rather than granitic under the oceans.

The rate of circulation of the deep ocean also has important implications for meteorology. The rate determines how effective the ocean is as an earth thermostat. If the rate is as slow as is indicated by these results, broad climatic fluctuations may be

detected since it might be expected that more water would sink near the Arctic and Antarctic regions during colder periods. Once the rate of circulation is established, a knowledge of the temperature of the water masses returning to the surface for any given future year might have important effects on the weather for that year. The sea/land ratio being so large particularly emphasizes the importance of such an effect.

It is concluded that major advances will be made in oceanography, and, to a lesser extent, in meteorology by the quantitative measurement of the rate of deep ocean circulation.

TABLE 2.
OCEAN WATER CARBON 14 MEASUREMENTS

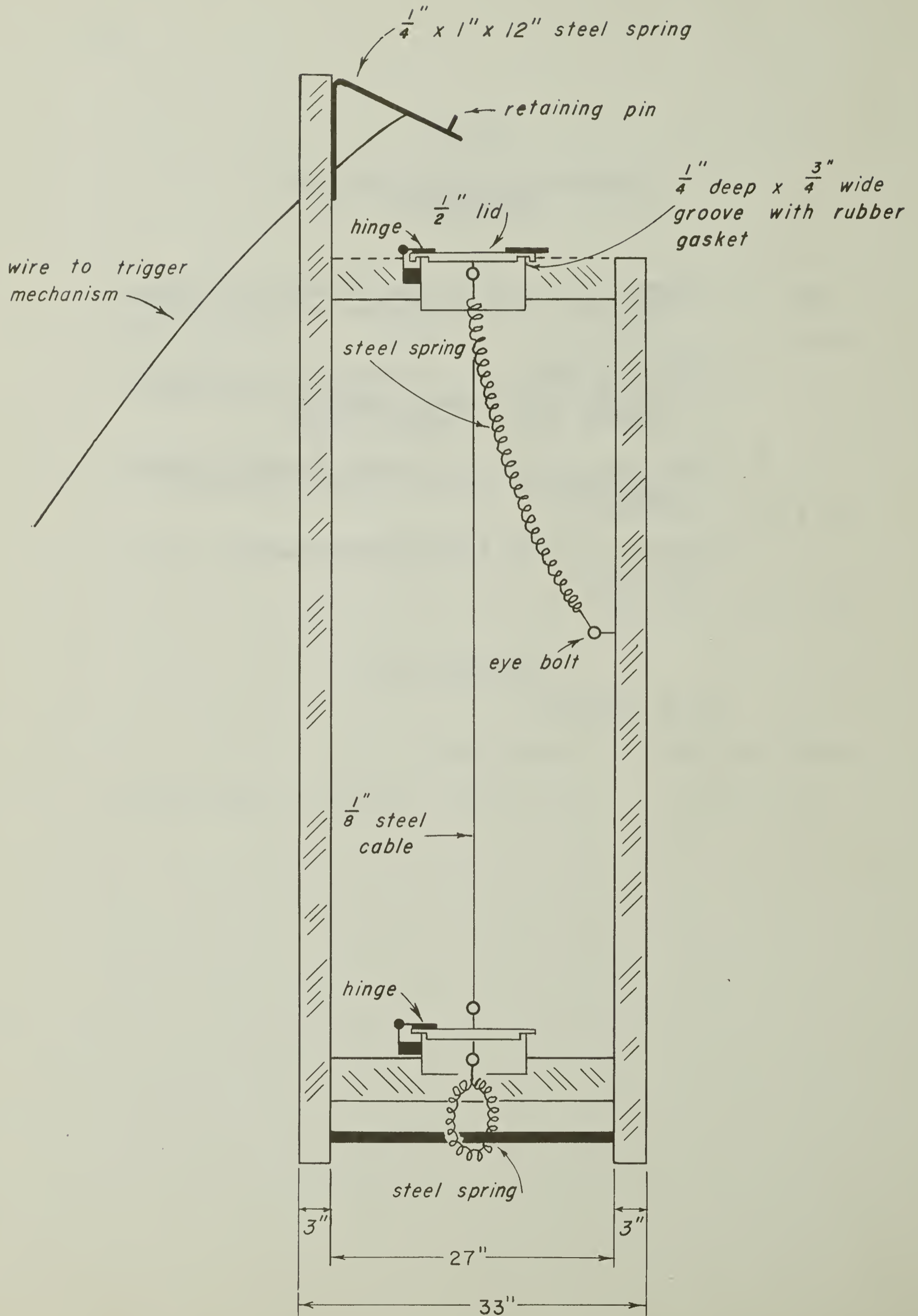
<u>Location</u>	<u>Depth</u>	<u>Cpm</u>	<u>Age</u>
54°35'W 41N	Surface	(1) 6.82 ± 0.09	Recent
		(2) 6.74 ± 0.07	
		Av. 6.77 ± 0.06	
		Average modern shells	
		6.72 ± 0.10	
58°19'N 32°56.8'W	1900 m	5.38 ± 0.07	1600 ± 130
		5.60 ± 0.11	
		Av. 5.45 ± 0.06	
53°526'N 21°06'W	2900 m	5.31 ± 0.12	1750 ± 150
		5.36 ± 0.12	
		Av. 5.34 ± 0.10	

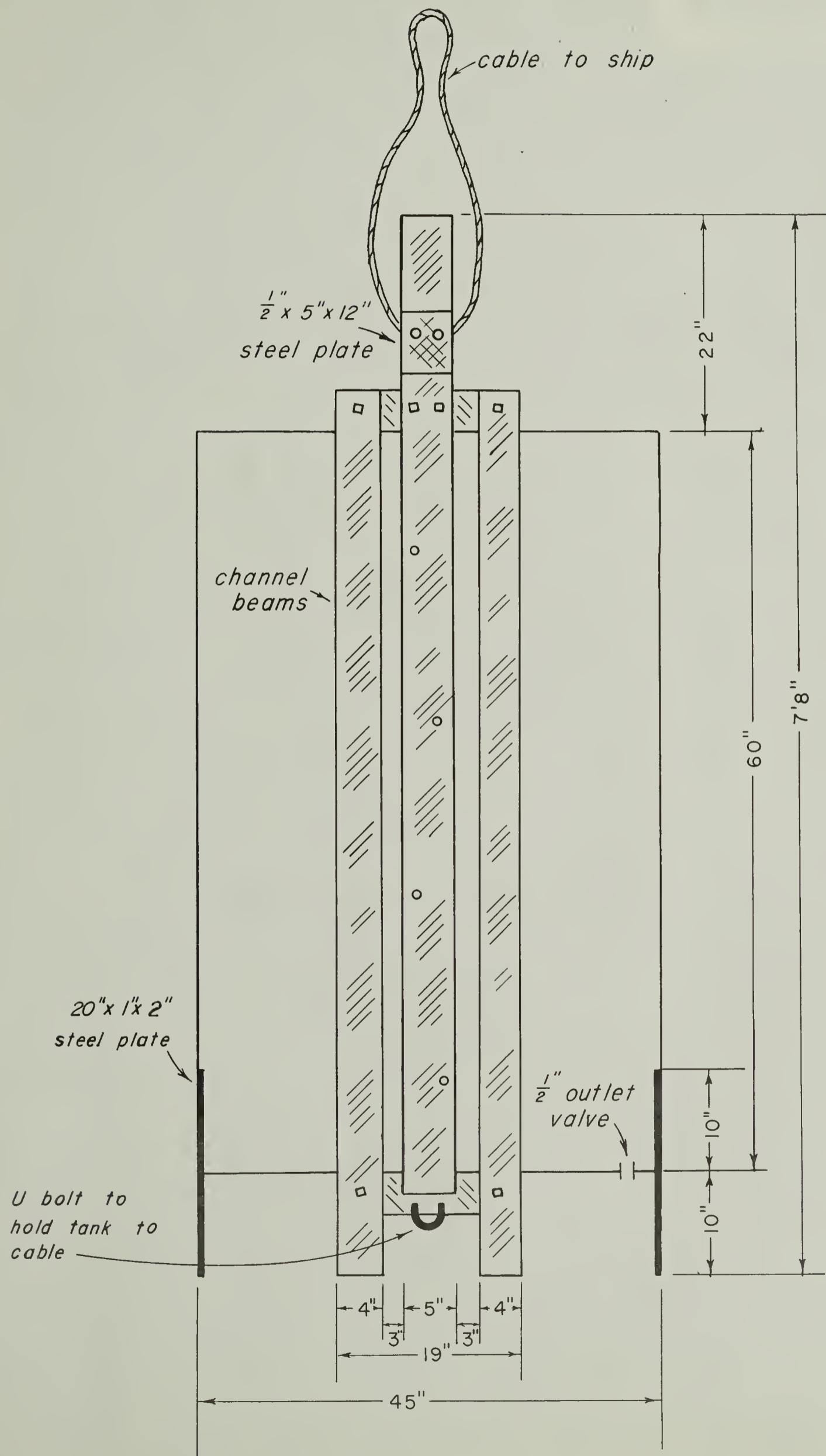
Direct Comparison

	<u>Difference in cpm</u>	
	From Averages	Direct Measurement
Surface sample vs. 58°19'N	1.32 ± 0.10	1.15 ± 0.12

BIBLIOGRAPHY

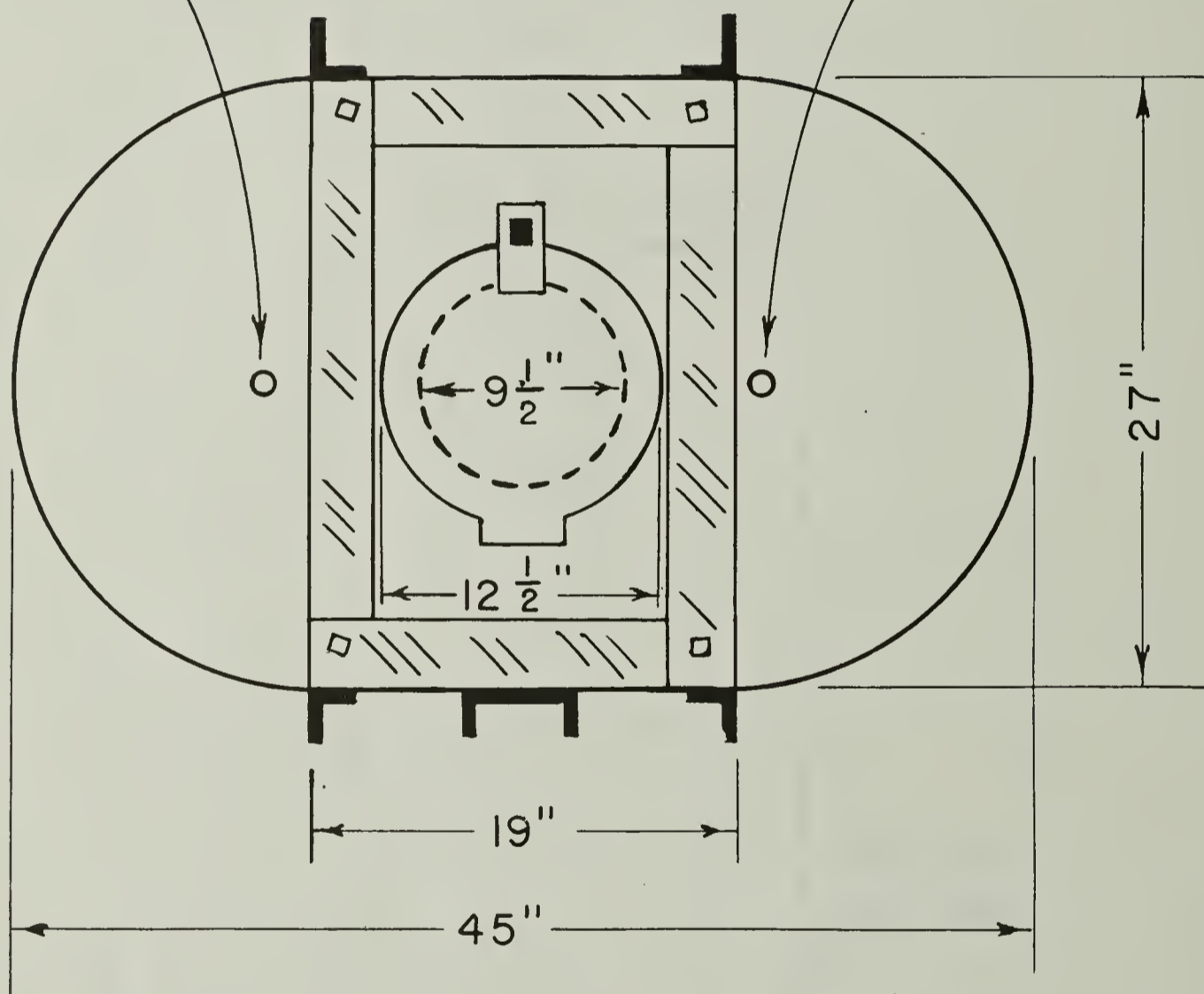
1. Anderson, E.C. and Libby, W.F., Worldwide distribution of natural radiocarbon, Phys. Rev. 81 pp. 64-69 (1951).
2. Kulp, J. L., Tryon, L.E., and Feely, H. W., Techniques of Natural Carbon 14 Determination, Trans. Am. Geophys. Union (in press for 1952).
3. Kulp, J. L., and Tryon, L.E., Extension of the Carbon 14 Age Method, Rev. Sci. Instr. (in press for 1952).
4. Kiersted, H., (1951) Personal Communication.





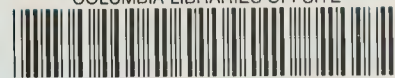
*inlet valve
for H₂SO₄*

*outlet valve
for CO₂*



TOP VIEW

COLUMBIA LIBRARIES OFFSITE



CU90424379

